

Advances in applying Laser Ablation ICPMS to paleoclimate research

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The combination of deep UV laser ablation and high sensitivity ICPMS in the mid-late 1990's provided an unprecedented advance in capability to measure trace element and isotopic compositional variations across μm to cm-scale growth banding in paleoproxy archives such as corals, speleothems, molluscs, foraminifers, otoliths, and teeth, among others. The speed, versatility, and ease of use of LA-ICPMS have underpinned subsequent rapid uptake and growth of applications by paleoclimate researchers until the present. Critical developments for paleoproxy applications include migrating to the use of deep ($\lambda < 200\text{nm}$) UV wavelengths which provide photon energies sufficient to achieve highly controlled photothermal ablation of calcite and other large band-gap materials. Another was design of dual-volume ablation cell technology to permit analysis of large samples with fast signal response and (thereby) higher spatial resolution. Together with improvements in mass spectrometry these developments have delivered exceptional sensitivity of analysis, and depth and surface compositional profiling and mapping capabilities, which have led to many novel and subsequent routine applications in paleoclimate research, and significant advances in our understanding of underlying biomineralization processes and how proxies work.

Current frontiers exist with further improving the spatial resolution and speed of analysis, developing cryogenic and other specialized sample cells to facilitate analysis of ice cores and other proxy archives, and achieving more efficient ion transmission and counting systems. Ongoing developments in multi-channel plate/array and faster, higher dynamic range detector technology are permitting more efficient and 'simultaneous' analysis of all elements/isotopes of interest using Time-of-Flight (TOF) and other mass spectrometers. Until now ultrafast femtosecond lasers have delivered minimal if any advantages over more conventional nanosecond lasers for analysing most paleoproxy archives because biocarbonates and bioapatites are insulating materials, with uptake limited to only 2-3% of total paleoclimate publications using LA-ICPMS. This may change with the availability of new, less costly, high-powered fiber femtosecond laser technology which, when coupled with TOF-MS or similarly capability, could provide high speed 2 and 3D compositional mapping of paleoproxy archives.